



DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/246,587 filed on November 8, 2000.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 24th day of January, 2001


Atsuko Ikeda

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

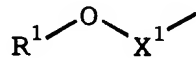
Novel Fumaric Acid Ester Derivative, Method for
Producing the Same, Polymerizable Composition
Containing the Same and Cured Product Thereof

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A fumaric acid ester derivative having a
group represented by formula (1) as the terminal groups and
having a group represented by formula (2) as a repeating
unit:

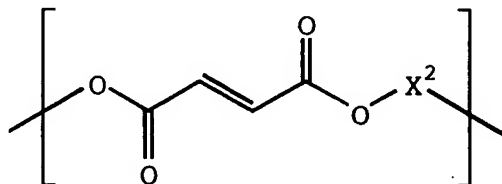
Formula (1)

[Chem. 1]



Formula (2)

[Chem. 2]

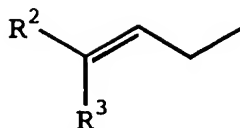


(wherein in formula (1), each R^1 independently represents
structural formula (1) or (2), and in formula (1) or (2), X^1
and X^2 each independently represents an organic residue
derived from a polyhydric alcohol having from 2 to 6
hydroxyl groups and 2 to 30 carbon atoms, provided that X^1
and X^2 may be ester-bonded to have a branched structure
having a group represented by formula (1) as the terminal

groups and having a group represented by formula (2) as a repeating unit);

Structural formula (1)

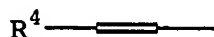
[Chem. 3]



(wherein R² and R³ each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms);

Structural formula (2)

[Chem. 4]

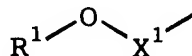


(wherein R⁴ represents hydrogen or an alkyl group having from 1 to 6 carbon atoms).

[Claim 2] A fumaric acid ester derivative having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) and/or formula (3) as a repeating unit:

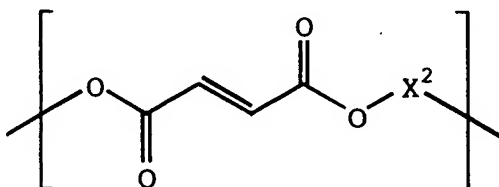
Formula (1)

[Chem. 5]



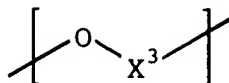
Formula (2)

[Chem. 6]



Formula (3)

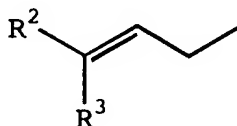
[Chem. 7]



(wherein in formula (1), each R^1 independently represents structural formula (1) or (2), and in formulae (1) to (3), X^1 , X^2 and X^3 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms, provided that X^1 , X^2 and X^3 may be ester-bonded or ether-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) and/or formula (3) as a repeating unit);

Structural formula (1)

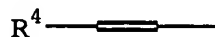
[Chem. 8]



(wherein R^2 and R^3 each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms);

Structural formula (2)

[Chem. 9]



(wherein R^4 represents hydrogen or an alkyl group having from 1 to 6 carbon atoms).

[Claim 3] The fumaric acid ester derivative as claimed in claim 1 or 2, wherein the number of repetitions of the repeating unit represented by formula (2) is any one in the range from 1 to 10.

[Claim 4] The fumaric acid ester derivative as claimed in claim 2 or 3, wherein the number of repetitions of the repeating unit represented by formula (3) is any one in the range from 1 to 5.

[Claim 5] The fumaric acid ester derivative as claimed in any one of claims 1 to 4, wherein 80% or more of R¹ in formula (1) is structural formula (2).

[Claim 6] The fumaric acid ester derivative as claimed in any one of claims 1 to 5, wherein R⁴ in structural formula (2) is any one or more selected from the group consisting of a methyl group, an ethyl group, an n-propyl group and an isopropyl group.

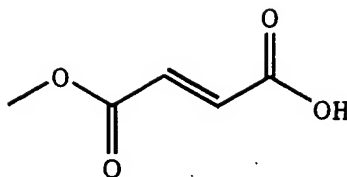
[Claim 7] The fumaric acid ester derivative as claimed in any one of claims 1 to 6, wherein X¹, X² and X³ in formulae (1) to (3) each independently is an organic residue derived from at least one alcohol selected from the group consisting of an alkylene diol, an alicyclic diol and an aromatic diol.

[Claim 8] The fumaric acid ester derivative as claimed in any one of claims 1 to 7, wherein at least one terminal group is a group represented by structural formula

(3):

Structural formula (3)

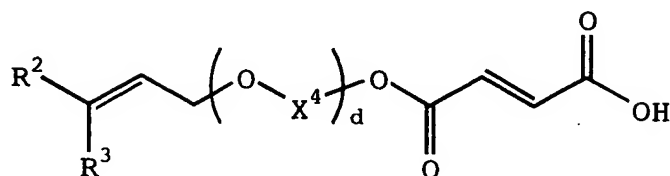
[Chem. 10]



[Claim 9] The fumaric acid ester derivative as claimed in claim 8, which is represented by formula (4):

Formula (4)

[Chem. 11]



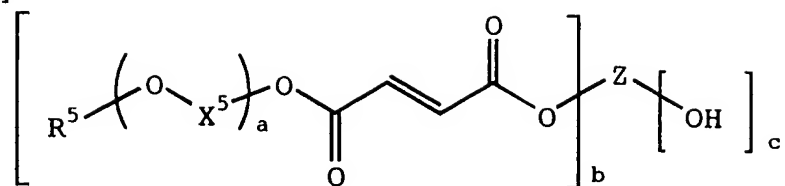
(wherein each X⁴, which is present in the number of d in formula (4), independently represents an alkylene group having from 2 to 4 carbon atoms or a cycloalkylene group having from 5 to 12 carbon atoms, d represents an integer of 1 to 5, and R² and R³ each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms).

[Claim 10] The fumaric acid ester derivative as claimed in any one of claims 1 to 9, wherein at least one terminal group is a hydroxyl group.

[Claim 11] The fumaric acid ester derivative as claimed in claim 10, which is represented by formula (5):

Formula (5)

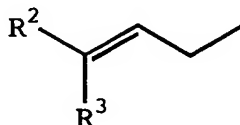
[Chem. 12]



(wherein Z represents an organic residue derived from a tri-, tetra-, hepta- or hexa-hydric alcohol, R⁵ represents structural formula (1) and/or structural formula (2), each X⁵, which is present in the number of a in formula (5), independently represents an alkylene group having from 2 to 4 carbon atoms or a cycloalkylene group having from 5 to 12 carbon atoms, a represents an integer of 1 to 5, b represents an integer of 1 to 6, c represents an integer of 0 to 5, and b+c is from 3 to 6);

Structural formula (1)

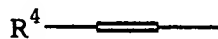
[Chem. 13]



(wherein R² and R³ each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms);

Structural formula (2)

[Chem. 14]



(wherein R⁴ represents hydrogen or an alkyl group having from 1 to 6 carbon atoms).

[Claim 12] A method for producing a fumaric acid ester derivative described in any one of claims 1 to 11, comprising reacting a fumaric acid ester derivative having at least one structural formula (3) in the terminal groups and having a group represented by formula (2) as a repeating unit with a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms in the presence of a catalyst.

[Claim 13] A method for producing a fumaric acid ester derivative described in any one of claims 1 to 11, comprising reacting a fumaric acid ester derivative having at least one structural formula (3) in the terminal groups and having a group represented by formula (2) as a repeating unit with a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms in the presence of sulfonyl chloride and a base.

[Claim 14] The method for producing a fumaric acid ester derivative as claimed in claim 12 or 13, wherein the polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms is at least one selected from the group consisting of trimethylolpropane, trimethylolethane, pentaerythritol, ditrimethylolpropane, dipentaerythritol and adducts thereof with an ethylene oxide or a propylene oxide.

[Claim 15] A method for producing a fumaric acid

ester derivative having structural formula (2) in the terminal groups, comprising isomerizing terminal groups of a fumaric acid ester derivative having structural formula (1) as the terminal groups in the presence of a catalyst to convert said terminal groups into structural formula (2).

[Claim 16] The method for producing a fumaric acid ester derivative having structural formula (2) in the terminal groups as claimed in claim 15, wherein the fumaric acid ester derivative having structural formula (1) as the terminal groups is the fumaric acid ester derivative described in any one of claims 1 to 11.

[Claim 17] The method for producing a fumaric acid ester derivative having structural formula (2) in the terminal groups as claimed in claim 15 or 16, wherein 80% or more of structural formula (1) in the fumaric acid ester derivative having structural formula (1) as the terminal groups is converted into structural formula (2) by the isomerization reaction.

[Claim 18] The method for producing a fumaric acid ester derivative having structural formula (2) in the terminal groups as claimed in any one of claims 15 to 17, wherein the catalyst used for the isomerization reaction is a catalyst containing at least one of palladium, rhodium and ruthenium.

[Claim 19] A polymerizable composition comprising the

fumaric acid ester derivative described in any one of claims 1 to 11.

[Claim 20] The polymerizable composition as claimed in claim 19, which comprises:

from 1 to 99% by mass of the fumaric acid ester derivative described in any one of claims 1 to 11, and

from 1 to 99% by mass of at least one compound selected from the group consisting of an unsaturated polyester, an oligomer having (meth)acrylate and a radical polymerizable monomer.

[Claim 21] A polymerizable composition comprising:

100 parts by mass of the polymerizable composition described in claim 19 or 20, and

from 0.01 to 15 parts by mass of a radical polymerization initiator.

[Claim 22] A cured product obtained by curing the polymerizable composition described in any one of claims 19 to 21.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a novel fumaric acid ester derivative having excellent radical polymerizability, capable of giving a polymer by light or heat, and usable as a crosslinking agent for various polymers, particularly

usable in the field where curing in air is required, such as coating material, coating, adhesive and sealing material, and also relates to a method for producing the derivative, a polymerizable composition containing the derivative, and a cured product thereof.

[0002]

[Background Art]

Heretofore, polyfunctional compounds having a double bond have been used for many uses, for example, as a starting material or the like of polymerizable compositions:

[0003]

These polymerizable compositions are cured predominantly by radical polymerization under light or heat. In particular, a high-speed photopolymerization by an ultraviolet ray (UV) is recently performed from the standpoint of profitability. The polymerizable composition used for the high-speed photopolymerization is generally an acrylic compound or an unsaturated carboxylic acid ester-base compound. However, these compounds have the following problems.

[0004]

The acrylic compound as a crosslinked monomer can be cured within a relatively short time in UV curing and therefore, is applied to various UV curing materials such as coating material and coating, however, this monomer has

a problem in that the skin irritation is relatively high and since the compound is prone to curing inhibition by oxygen, stickiness is readily generated at the formation of a thin film.

[0005]

With respect to the unsaturated carboxylic acid ester-type compound, dialkyl esters of fumaric acid or maleic acid are known, however, these compounds are individually poor in the radical polymerization property and even when copolymerized with another resin, the degree of crosslinking is not sufficiently high and the cured product obtained may suffer from insufficient strength in some cases. Furthermore, the unsaturated polyester by itself has a large molecular weight and is poor in the homopolymerizability, therefore, a styrene monomer is generally used as a reactive diluent. However, in view of workability such as odor, an alternative of the styrene monomer is demanded.

[0006]

In order to overcome these problems, vinyl ethers as one of alkenyl ethers are recently taken notice of as a non-acrylic compound.

[0007]

The vinyl ethers are generally used as a curable material for cationic polymerization system. It is said that radical polymerization of the vinyl ether itself

scarcely proceeds when used alone, however, a report in Rad. Tech. North America, 167 (1992) states that copolymerization proceeds between maleic acid ester and vinyl ether.

[0008]

Other than this, some examples of copolymerization systems are also known. U.S. Patents 5,334,455 and 5,334,456 describe a system where a polyfunctional vinyl ether is polymerized with a reactant between epoxy and maleic anhydride and a system where a polyfunctional vinyl ether is polymerized with a maleic acid ester, and Japanese Patent 2,705,916 describes a composition of an unsaturated polyester and a vinyl ether.

[0009]

In addition, the vinyl ether is known to copolymerize with an acrylate despite its low copolymerizability.

[0010]

The vinyl ether is characterized by low viscosity, excellent diluting ability and high adhesion to a substrate at the curing but, as described above, exhibits poor radical polymerizability when used alone. Therefore, in the system where an unsaturated polyester or the like is blended, the vinyl ether group is incompletely polymerized to fail in bringing out the physical properties of the cured product and furthermore, the ratio of the other polymerizable group to the vinyl ether group in the

polymerization must be adjusted, giving rise to a problem that the amount of vinyl ether used is limited.

[0011]

In order to overcome these problems, JP-B-55-395533 (the term "JP-B" as used herein mean an "examined Japanese patent publication") describes a method for producing a compound having a vinyl ether group at the terminal and having a maleate structure in the inside, and British Patent 1,188,112 describes a compound having an allyl ether group at the terminal and having a maleate or fumarate structure in the inside.

[0012]

These polymerizable compounds have, however, only two polymerizable groups at the terminal and one polymerizable group in the inside and still cannot have a sufficiently large number of crosslinking points.

[0013]

[Problems to be solved by the Invention]

The object of the present invention is to provide a novel fumaric acid ester derivative which can overcome the problems in conventional radical polymerizable compounds, such as curing inhibition by oxygen at curing or low surface hardness of the cured product, and which has a sufficiently large number of crosslinking points. The object of the present invention includes providing a method

for producing the derivative, a polymerizable composition containing the derivative, and a cured product thereof.

[0014]

[Means to Solve the Problems]

As a result of extensive investigations to solve the above-described problems, the present inventors have found a novel fumaric acid ester derivative polyfunctionalized to have an alkenyloxy group such as vinyl ether group, propenyl ether group or allyl ether group, and a fumarate group within the same molecule and further having many double bonds. The above-described objects can be attained by using this fumaric acid ester derivative as a radical polymerizable resin or a crosslinking agent for resin. The present invention has been accomplished based on this finding.

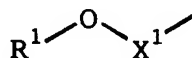
[0015]

More specifically, the present invention (I) is a fumaric acid ester derivative having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) as a repeating unit:

[0016]

Formula (1)

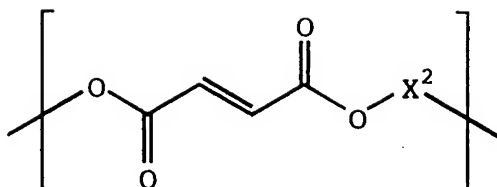
[Chem. 15]



[0017]

Formula (2)

[Chem. 16]



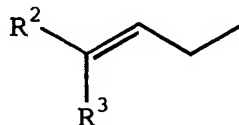
[0018]

(wherein in formula (1), each R^1 independently represents structural formula (1) or (2), and in formula (1) or (2), X^1 and X^2 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and 2 to 30 carbon atoms, provided that X^1 and X^2 may be ester-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) as a repeating unit);

[0019]

Structural formula (1)

[Chem. 17]



[0020]

(wherein R^2 and R^3 each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms);

[0021]

Structural formula (2)

[Chem. 18]



[0022]

(wherein R^4 represents hydrogen or an alkyl group having from 1 to 6 carbon atoms).

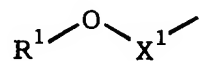
[0023]

The present invention (II) is a fumaric acid ester derivative having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) and/or formula (3) as a repeating unit:

[0024]

Formula (1)

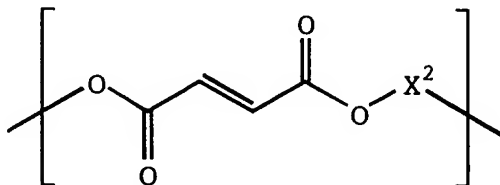
[Chem. 19]



[0025]

Formula (2)

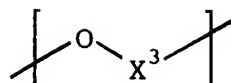
[Chem. 20]



[0026]

Formula (3)

[Chem. 21]



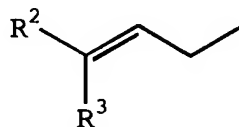
[0027]

(wherein in formula (1), each R^1 independently represents structural formula (1) or (2), and in formulae (1) to (3), X^1 , X^2 and X^3 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms, provided that X^1 , X^2 and X^3 may be ester-bonded or ether-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) and/or formula (3) as a repeating unit);

[0028]

Structural formula (1)

[Chem. 22]



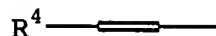
[0029]

(wherein R^2 and R^3 each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms);

[0030]

Structural formula (2)

[Chem. 23]



[0031]

(wherein R^4 represents hydrogen or an alkyl group having from 1 to 6 carbon atoms).

[0032]

The present invention (III) is a method for producing the fumaric acid ester derivative of the present invention (I) or (II).

[0033]

The present invention (IV) is a polymerizable composition comprising the fumaric acid ester derivative of the present invention (I) or (II).

[0034]

The present invention (V) is a cured product obtained by curing the polymerizable composition of the present invention (IV).

[0035]

[Mode for Carrying Out the Invention]

The present invention is described below.

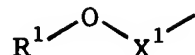
The present invention (I) is described. The present invention (I) is a fumaric acid ester derivative having a group represented by formula (1) as the terminal groups and

having a group represented by formula (2) as a repeating unit:

[0036]

Formula (1)

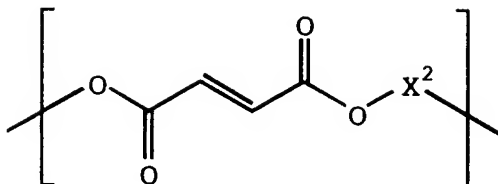
[Chem. 24]



[0037]

Formula (2)

[Chem. 25]



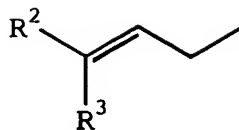
[0038]

(wherein in formula (1), each R^1 independently represents structural formula (1) or (2), and in formula (1) or (2), X^1 and X^2 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and 2 to 30 carbon atoms, provided that X^1 and X^2 may be ester-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) as a repeating unit);

[0039]

Structural formula (1)

[Chem. 26]



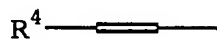
[0040]

(wherein R² and R³ each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms);

[0041]

Structural formula (2)

[Chem. 27]



[0042]

(wherein R⁴ represents hydrogen or an alkyl group having from 1 to 6 carbon atoms).

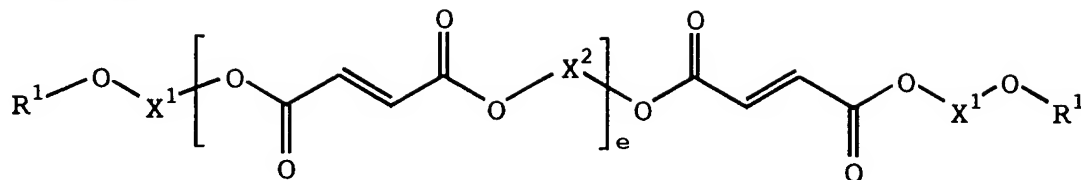
[0043]

The present invention (I) has at least one group represented by formula (1) in the terminal groups and containing a fumaric acid ester structure represented by formula (2) in one or more repeating unit. Representative examples thereof include a compound represented by formula (6):

[0044]

Formula (6)

[Chem. 28]



[0045]

(wherein e represents an integer of 0 to 9).

[0046]

R^1 in formula (1) according to the present invention represents either structural formula (1) or structural formula (2).

[0047]

In structural formula (1), R^2 and R^3 each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms. In structural formula (1), in view of the radical polymerizability, preferred is the case where at least one of R^2 and R^3 is hydrogen or a methyl group and the other is at least one of hydrogen, a methyl group, an ethyl group, an *n*-propyl group and an isopropyl group, more preferred is the case where at least one of R^2 and R^3 is hydrogen and the other is hydrogen or a methyl group, and most preferred is the case where both R^2 and R^3 are hydrogen. With an alkyl group having 4 or more carbon atoms, the polymerizability may disadvantageously decrease.

[0048]

In structural formula (2), R^4 represents hydrogen or an alkyl group having from 1 to 6 carbon atoms. In structural formula (2), in view of the radical polymerizability, R^4 is preferably at least one of hydrogen, a methyl group, an ethyl group, an n-propyl group and an isopropyl group, more preferably hydrogen or a methyl group. With an alkyl group having 4 or more carbon atoms, the polymerizability may disadvantageously decrease.

[0049]

X^1 and X^2 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms.

[0050]

Specific examples of the polyhydric alcohol include alkylene diols and polyalkylene diols, such as ethylene glycol, neopentyl glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and nonanediol; alicyclic diols such as 1,1-cyclohexanediol, 1,2-cyclohexanediol, 1,3-cyclohexanediol, 1,4-cyclohexanediol, 1,1-cyclohexanedimethanol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol and tricyclodecanedimethanol; and aromatic diols such as bisphenol A, ethylene oxide adduct of bisphenol A, propylene oxide adduct of bisphenol A,

bisphenol F, ethylene oxide adduct of bisphenol F, propylene oxide adduct of bisphenol F and benzenedimethanol.

[0051]

Also, trihydric alcohols such as trimethylolethane, trimethylolpropane and glycerol; tetrahydric alcohols such as pentaerythritol, diglycerol and ditrimethylolpropane; hexahydric alcohols such as dipentaerythritol and sorbitol; and ethylene oxide adducts and propylene oxide adducts of these polyhydric alcohols may be added to an extent not to cause gelation.

[0052]

Among these, X^1 is preferably an alkylene group having from 2 to 4 carbon atoms, such as ethylene group $-(CH_2)_2-$, 1,3-propylene group $-(CH_2)_3-$ and 1,2-propylene group $(-CH_2-CH(CH_3)-)$,

[0053]

a 1,1-cyclohexylene group, a 1,2-cyclohexylene group, a 1,3-cyclohexylene group, a 1,4-cyclohexylene group,

[0054]

or a cycloalkylene having from 6 to 8 carbon atoms, such as organic residue derived from 1,1-cyclohexanedimethanol, organic residue derived from 1,2-cyclohexanedimethanol, organic residue derived from 1,3-cyclohexanedimethanol or organic residue derived from 1,4-cyclohexanedimethanol, represented by formula $(-CH_2-C_6H_{10}-CH_2-)$, because

excellent results can be obtained in view of hardness of the cured product after the polymerization.

[0055]

The number of the repeating units of formula (2) may be one or more but is preferably from 1 to 10 (e in formula (6) is an integer of 0 to 9). If the number of repeating units exceeds 10, the viscosity excessively increases and gelation may disadvantageously occur at the time of production.

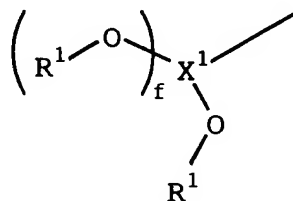
[0056]

In the case where X^1 is an organic residue derived from a trihydric or greater polyhydric alcohol, X^1 may also have a branched structure represented by the following structural formula (6):

[0057]

Structural formula (6)

[Chem. 29]



[0058]

(wherein f represents an integer of 0 to 4).

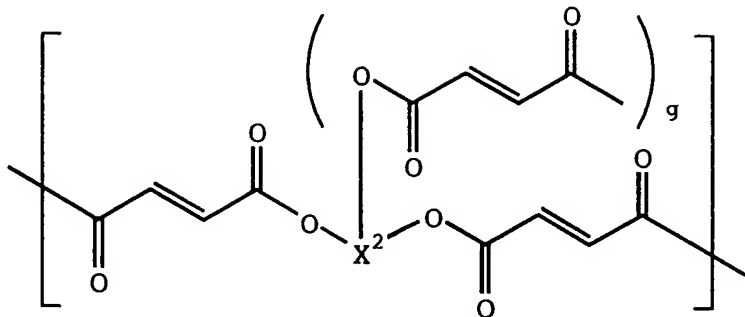
In the case where X^2 is an organic residue derived from a trihydric or greater polyhydric alcohol, X^2 may also

have a branched structure represented by the following structural formula (7):

[0059]

Structural formula (7)

[Chem. 30]



[0060]

(wherein g represents an integer of 0 to 4).

[0061]

R¹ as a polymerizable group at the terminal of formula (1) is by itself poor in the radical polymerizability and curing thereof proceeds in the polymerization with a fumaric acid ester group, therefore, when the molar ratio of R¹ group/fumarate group is close to 1, the cured product can have excellent physical properties. The molar ratio of R¹ group/fumarate group is preferably from 0.2 to 2, more preferably from 0.8 to 1.5.

[0062]

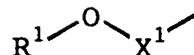
The present invention (II) is described below. The present invention (II) is a fumaric acid ester derivative having a group represented by formula (1) as the terminal

groups and having a group represented by formula (2) and/or represented by formula (3) as a repeating unit:

[0063]

Formula (1)

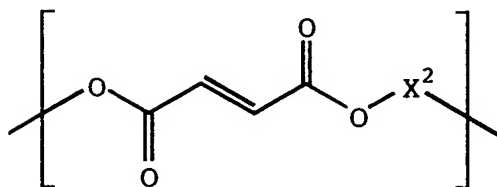
[Chem. 31]



[0064]

Formula (2)

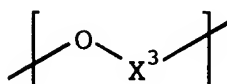
[Chem. 32]



[0065]

Formula (3)

[Chem. 33]



[0066]

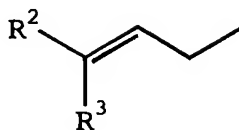
(wherein in formula (1), each R^1 independently represents structural formula (1) or (2), and in formulae (1) to (3), X^1 , X^2 and X^3 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms, provided that X^1 , X^2 and X^3 may be ester-bonded or ether-bonded to have a branched structure having a group

represented by formula (1) as the terminal groups and having a group represented by formula (2) and/or formula (3) as a repeating unit);

[0067]

Structural formula (1)

[Chem. 34]



[0068]

(wherein R² and R³ each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms);

[0069]

Structural formula (2)

[Chem. 35]



[0070]

(wherein R⁴ represents hydrogen or an alkyl group having from 1 to 6 carbon atoms).

[0071]

The fumaric acid ester derivative of the present invention (II) has at least one group represented by formula (1) as the terminal groups and contains an ether structure represented by formula (3) as a repeating structure in addition to the fumaric acid ester structure represented by formula (2).

[0072]

In the present invention (II), the terminal group represented by formula (1) and the repeating structure represented by formula (2) are the same as those in the present invention (I).

[0073]

X³ contained in formula (3) represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms similarly to X¹ of formula (1) and X² of formula (2).

[0074]

X³ is also the same as X¹ of formula (1) and X² of formula (2) in the preferred polyhydric alcohol and in the point that X³ can have a branch structure.

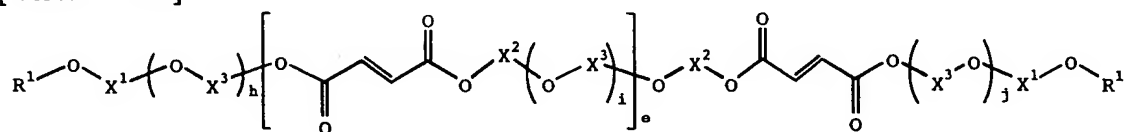
[0075]

One representative example of the fumaric acid ester derivative of the present invention (II) is a compound represented by the following formula (7):

[0076]

Formula (7)

[Chem. 36]



[0077]

(wherein h, i and j each represents an integer of 0 to 5,

and e represents an integer of 1 to 9, provided that $h+i+j \geq 1$).

[0078]

h, i and j each is an integer of 0 to 5. If any one of h, i and j exceeds 5, the concentration of the polymerizable double bond decreases to cause reduction in the curability or hardness of the cured product and this is not preferred.

[0079]

The fumaric acid ester derivatives of the present invention (I) and the present invention (II) necessarily have one or more group represented by formula (1) as a terminal group and may also partially have a carboxyl group represented by formula (3) derived from fumaric acid or a hydroxyl group derived from a polyhydric alcohol, as a terminal group.

[0080]

Specific examples of the fumaric acid ester derivative having a carboxyl group represented by formula (3) derived from fumaric acid as a terminal group include a compound represented by formula (4).

[0081]

The fumaric acid ester derivative represented by formula (4) is a polymerizable compound having an allyl ether group and a carboxylic acid group derived from

fumaric acid as the terminal groups and having a fumarate skeleton in the inside thereof. The allyl ether group and the fumarate group have high radical copolymerizability. The carboxylic acid group at the terminal can form an ester bond with various hydroxyl groups and can synthesize polymerizable ester derivatives having various physical properties.

[0082]

Specific examples of the compound having a hydroxyl group as a terminal group include a compound represented by formula (5).

[0083]

Formula (5) is a fumaric acid ester derivative having either one of the allyl ether group represented by structural formula (1) and the propenyl ether group represented by structural formula (2) as a terminal group and at the same time, having a hydroxyl group derived from a polyhydric alcohol as a terminal group. In formula (5), Z represents an organic residue derived from a tri-, tetra-, penta- or hexa-hydric alcohol.

[0084]

Examples of the polyhydric alcohol as used herein include trihydric alcohols such as trimethylolpropane, trimethylolethane and glycerol; tetrahydric alcohols such as pentaerythritol, ditrimethylolpropane and diglycerol;

hexahydric alcohols such as sorbitol and dipentaerythritol; adducts of ethylene oxide or propylene oxide to the hydroxyl group of these tri-, tetra-, hepta- and hexahydric alcohols; and mixtures of two or more thereof.

[0085]

Among these, trimethylolpropane, trimethylolethane, pentaerythritol, ditrimethylolpropane, dipentaerythritol (in these compounds, all hydroxyl group valences are primary alcohol), ethylene oxide adducts of these alcohols, and mixtures of two or more thereof are preferred because of their high reactivity in the esterification reaction.

[0086]

The present invention (III) is described below. The present invention (III) is a method for producing the fumaric acid ester derivative of the present invention (I) or (II).

[0087]

The method for producing a fumaric acid ester derivative of the present invention (I) or (II) can be divided into the following two steps A) and B), namely,

A) a step of forming an ester as the main skeleton of the fumaric acid ester derivative and forming a repeating unit of the ester, and

B) a step of forming a polymerizable group at terminals by isomerization.

[0088]

These two steps are not essential in producing the fumaric acid ester derivative of the present invention (I) or (II) and only through either one step, the fumaric acid ester derivative of the present invention (I) or (II) can be produced.

[0089]

The step A) in the production method of the fumaric acid ester derivative of the present invention (I) or (II) is described below.

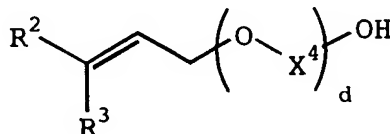
[0090]

The fumaric acid ester derivative represented by formula (4) of the present invention (I) can be produced by a method of performing an addition-reaction between a maleic anhydride and an alcohol represented by formula (8) to obtain a maleic acid monoester and then isomerizing the ester from maleate into fumarate:

[0091]

Formula (8)

[Chem. 37]



[0092]

(wherein X⁴ represents an alkylene group having from 2 to 4

carbon atoms or a cycloalkylene group having from 5 to 12 carbon atoms, d represents an integer of 1 to 5, and R² and R³ each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms).

[0093]

The fumaric acid ester derivative represented by formula (5) of the present invention (I), where R⁵ is structural formula (1), can be produced by an esterification reaction of the fumaric acid ester derivative represented by formula (4) with a polyhydric alcohol.

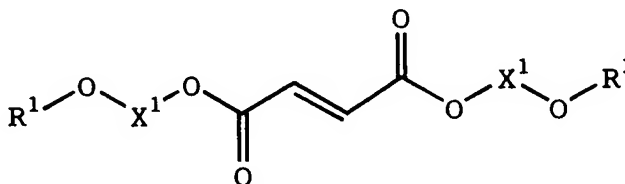
[0094]

Furthermore, the fumaric acid ester derivative represented by formula (6) of the present invention (I), where R¹ is structural formula (1), can be produced by a transesterification reaction between a fumaric acid ester derivative represented by formula (9) and a polyhydric alcohol.

[0095]

Formula (9)

[Chem. 38]



[0096]

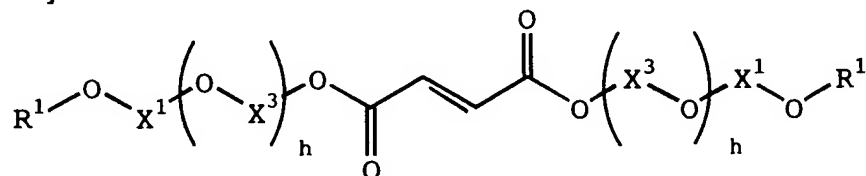
(wherein each R^1 independently represents structural formula (1) or (2), and X^1 represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms).

The fumaric acid ester derivative represented by formula (7) of the present invention (II), where R^1 is structural formula (1), can be produced by a transesterification reaction between a fumaric acid ester derivative represented by formula (10) and a polyhydric alcohol represented by formula (11):

[0097]

Formula (10)

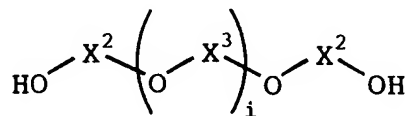
[Chem. 39]



[0098]

Formula (11)

[Chem. 40]



[0099]

The method for producing the fumaric acid ester derivative represented by formula (4) is described in

detail below. Specific examples of the method for producing the fumaric acid ester derivative represented by formula (4) include a method of performing an addition-reaction between a maleic anhydride and an alcohol represented by formula (8) to obtain a maleic acid monoester and then isomerizing the ester from maleate to fumarate.

[0100]

The addition reaction of a maleic anhydride and an alcohol represented by formula (8) can be performed in the presence or absence of a catalyst. The catalyst is not particularly limited as long as it is a general esterification catalyst but preferred examples thereof include basic catalysts such as triethylamine and N,N-dimethylaminopyridine.

[0101]

The reaction is performed at a temperature of 20 to 100°C, preferably from 40 to 80°C. If the reaction temperature is less than 20°C, the reaction proceeds slowly and unnecessarily takes a time and this is not preferred, whereas if the reaction temperature exceeds 100°C, the amount of diester produced increases and the yield disadvantageously decreases.

[0102]

The ratio of the amount charged of the maleic anhydride to the amount charged of the alcohol represented

by formula (8) is not particularly limited. The alcohol represented by formula (8) is generally from 0.2 to 10 equivalents in mol, preferably from 0.5 to 5 equivalents in mol, more preferably from 0.9 to 2 equivalents in mol, to 1 mol of the maleic anhydride.

[0103]

If the ratio of the amount charged of the alcohol represented by formula (8) exceeds 10 equivalents in mol, excess alcohol increases, whereas if the ratio is less than 0.2 equivalents in mol, unreacted maleic anhydride increases and this is not preferred in view of profitability.

[0104]

In this addition reaction, a solvent may be added. Examples of the solvent include aromatic hydrocarbons such as benzene, toluene and xylene, and ethers such as diethyl ether, dimethoxyethane, methoxy ethyl ether, tetrahydrofuran and 1,4-dioxane.

[0105]

In the alcohol represented by formula (8), R^2 and R^3 each independently represents hydrogen or an alkyl group having from 1 to 5 carbon atoms, similarly to R^2 and R^3 in structural formula (1).

[0106]

In the alcohol, R^2 and R^3 both are preferably hydrogen

in view of the polymerizability. Specific examples of the alcohol represented by formula (8) include ethylene glycol monoallyl ether, propylene glycol monoallyl ether, 1,3-butylene glycol monoallyl ether, 1,4-butylene glycol monoallyl ether, cyclohexanediol monoallyl ether, cyclohexanedimethanol monoallyl ether, diethylene glycol monoallyl ether and dipropylene glycol monoallyl ether.

[0107]

The obtained maleic acid monoester can be isomerized into a fumaric acid monoester using a catalyst such as thiourea, chlorine, bromine, iodine or acid chloride, in the presence of a known acidic catalyst such as hydrochloric acid, or a basic catalyst such as morpholine, piperidine or diethylamine.

[0108]

The reaction temperature in the isomerization reaction is not particularly limited and is generally from 30 to 200°C, preferably from 50 to 150°C, more preferably from 70 to 120°C. If the reaction temperature exceeds 200°C, the polymerization or decomposition reaction disadvantageously bears higher danger.

[0109]

In this isomerization reaction, a known hindered phenol-base polymerization inhibitor or a solvent may be used. Examples of the solvent used herein include aromatic

hydrocarbons such as benzene, toluene and xylene; ethers such as diethyl ether, dimethoxyethane, methoxy ethyl ether, tetrahydrofuran and 1,4-dioxane; esters such as ethyl acetate and butyl acetate; ketones such as acetone and methyl ethyl ketone.

[0110]

The fumaric acid ester derivative represented by formula (4) obtained as such can be purified by a treatment such as distillation or liquid separation.

[0111]

The method for producing the fumaric acid ester derivative represented by formula (5) where R^5 is structural formula (1) is described below.

[0112]

The fumaric acid ester derivative represented by formula (5) where R^5 is structural formula (1) can be produced by an esterification reaction of the fumaric acid ester derivative represented by formula (4) and a polyhydric alcohol. Specific examples of the esterification reaction include the following three methods:

[0113]

① a method of esterifying the fumaric acid ester derivative represented by formula (4) and a polyhydric alcohol in the presence of an acid catalyst,

② a method of inducing the fumaric acid ester

derivative represented by formula (4) into an acid halide and then reacting it with a polyhydric alcohol to perform the esterification, and

③ a method of reacting the fumaric acid ester derivative represented by formula (4) with a polyhydric alcohol using a condensing agent to perform the esterification.

[0114]

The method ① is described below.

Examples of the esterification catalyst which can be used in the method ① include known catalysts such as sulfuric acid, p-toluenesulfonic acid, methanesulfonic acid, ion exchange resin, a mixed catalyst of boric acid and sulfuric acid, polyphosphoric acid and Lewis acid (e.g., boron trifluoride etherate).

[0115]

The reaction can be performed under atmospheric pressure, applied pressure or reduced pressure, for example, at 15 Pa to 1 MPa in terms of an absolute pressure. The reaction temperature is from 20 to 200°C, preferably from 40 to 150°C, and the reaction is performed while distilling off water generated as a by-product. If the reaction temperature is less than 20°C, the reaction proceeds slowly, whereas if it exceeds 200°C, by-products such as polymerization product may increase.

[0116]

At the reaction, a solvent may be used. The solvent used is not particularly limited and specific examples thereof include benzene, hexane, cyclohexane, toluene and xylene.

[0117]

The charging ratio of the fumaric acid derivative represented by formula (4) to a polyhydric alcohol is not particularly limited but these are preferably charged such that the hydroxyl group (-OH) of the polyhydric alcohol is from 0.2 to 5 equivalents in mol, more preferably from 0.5 to 1.5 equivalents in mol, to the carboxyl group (-COOH) of the fumaric acid ester derivative represented by formula (4). If the charging ratio is less than 0.2 equivalents in mol, the residual amount of the fumaric acid ester derivative represented by formula (4) is excessively large, whereas if it exceeds 5 equivalents in mol, unreacted hydroxyl group disadvantageously remains.

[0118]

Depending on the reaction conditions, for example, the alcohol corresponding to $R^5-(OX^5)_a-OH$ may be partly desorbed from the ester position of the fumaric acid ester derivative represented by formula (5), this alcohol causes an esterification reaction with the carboxyl group of the fumaric acid ester derivative represented by formula (4) to

produce a diester monomer of fumaric acid, and the monomer is contained in the product in some cases, however, the product can be used as a polymerizable composition without removing the monomer.

[0119]

After the completion of esterification reaction, purification may also be performed for removing the impurities or unreacted matters. The purification may be performed, for example, by dissolving a fumaric acid ester derivative in an organic solvent such as benzene, toluene, cyclohexane, diethyl ether, methyl acetate or ethyl acetate, washing the solution with water or alkali, and thereby removing the unreacted fumaric acid ester derivative represented by formula (4) or carboxylic acids as by-product, in the form of a salt.

[0120]

The purity may also be increased by a method of subjecting the product to decantation or reprecipitation with an organic solvent such as aliphatic hydrocarbons (e.g., hexane, octane), by a method of purifying the product through a column using silica gel or by thin layer chromatography.

[0121]

The method ② is described below.

The method ② is a method of inducing the fumaric acid

ester derivative represented by formula (4) into an acid halide and then reacting it with a polyhydric alcohol to perform the esterification.

[0122]

In the method ②, the method of inducing the fumaric acid ester derivative represented by formula (4) into an acid halide is not particularly limited and a known method using thionyl chloride, phosphoryl chloride, phosphorus pentachloride, phosphorus trichloride or phosgene may be used.

[0123]

Particularly, in the case where thionyl chloride is used, zinc chloride, pyridine, iodine or triethylamine may be used in combination as a catalyst. Also, a mixture of thionyl chloride and dimethylformamide and a mixture of thionyl chloride and hexamethylphosphoric triamide is known to be a good reagent for synthesizing the acid halide.

[0124]

By reacting the thus-induced acid halide of the fumaric acid ester derivative represented by formula (4) with a polyhydric alcohol using a known method, the fumaric acid ester derivative represented by formula (5) of the present invention can be produced.

[0125]

The method ③ is described below.

The method ③ is a method of reacting the fumaric acid ester derivative represented by formula (4) with a polyhydric alcohol using a condensing agent to perform the esterification.

[0126]

Specific examples of the condensing agent for use in the method ③ include dicyclohexylcarbodiimide, trifluoroacetic anhydride and sulfonyl chloride, however, the present invention is not limited thereto. Any commonly known condensing agent may be used without any limit.

[0127]

Among these, a method of using sulfonyl chloride is preferred in view of easy handleability. Examples of the case where sulfonyl chloride is used as the condensing agent include a method of adding a base to the fumaric acid ester derivative represented by formula (4) in the presence of a solvent, followed by the reaction, adding sulfonyl chloride and finally adding a polyhydric alcohol, followed by the reaction.

[0128]

Examples of the sulfonyl chloride used here include p-toluenesulfonyl chloride, methanesulfonyl chloride and trifluoromethanesulfonyl chloride.

[0129]

The charging amounts of the fumaric acid ester

derivative represented by formula (4) and the sulfonyl chloride are not particularly limited, however, sulfonyl chloride in equivalent or more is generally used. The sulfonyl chloride is preferably charged in an amount of 1 to 2 equivalents in mol to the fumaric acid ester derivative represented by formula (4).

[0130]

The charging ratio of the fumaric acid ester derivative represented by formula (4) and a polyhydric alcohol is not particularly limited. These are preferably charged such that the hydroxyl group (-OH) of the polyhydric alcohol is from 0.2 to 2 equivalents in mol, more preferably from 0.4 to 1.2 equivalents in mol, to the carboxyl group (-COOH) of the fumaric acid ester derivative represented by formula (4).

[0131]

The solvent used here is not particularly limited as long as it does not inhibit the reaction. Specific examples thereof include ethers such as tetrahydrofuran and dioxane; aromatic hydrocarbons such as benzene, toluene and xylene; halides such as chloroform, dichloromethane and dichloroethane; dimethylformamide; and dimethylsulfoxide.

[0132]

Examples of the base include alkali metals such as sodium hydroxide, potassium hydroxide, cesium hydroxide,

sodium carbonate, potassium carbonate, cesium carbonate, sodium hydrogencarbonate and potassium hydrogencarbonate.

[0133]

The amount of the base varies depending on the kind thereof, however, is preferably from 1 to 5 equivalents in mol to the fumaric acid ester derivative represented by formula (4).

[0134]

The reaction temperature is from -20 to 100°C, preferably from 0 to 50°C. If the reaction temperature exceeds 100°C, the side reaction increases, whereas if it is less than -20°C, the reaction may be disadvantageously delayed.

[0135]

The product obtained can be purified for removing impurities. Examples of the purification method include a method of dissolving the product in an organic solvent such as benzene, toluene, xylene, cyclohexane, methyl acetate, ethyl acetate, diethyl ether, dichloroethane or chloroform, and then washing the solution with water, alkali or acid; a method of subjecting the product to decantation or reprecipitation with an organic solvent such as aliphatic hydrocarbon (e.g., hexane, octane). The purity may also be enhanced by column purification using silica gel or thin layer chromatography.

[0136]

The method for producing the fumaric acid ester derivative represented by formula (6) of the present invention (I), where R¹ is structural formula (1), is described below.

[0137]

The fumaric acid ester derivative represented by formula (6) of the present invention (I), where R¹ is structural formula (1), can be produced by a transesterification reaction between the fumaric acid ester derivative represented by formula (9) and a polyhydric alcohol. More specifically, the fumaric acid ester derivative represented by formula (6) where R¹ is structural formula (1) can be produced by a method of reacting the fumaric acid ester derivative represented by formula (9) with a polyhydric alcohol in the presence of a known transesterification catalyst while removing alcohol generated as a by-product.

[0138]

The transesterification catalyst which can be used here is not particularly limited. Specific examples thereof include alkali metals, alkaline earth metals, oxides thereof, oxides and hydroxides of Zn, Sn and Ti, alcoholates, and acetylacetonate complexes.

[0139]

The reaction temperature is 80 to 200°C and the reaction may be performed under atmospheric pressure, applied pressure or reduced pressure, for example, at 15 Pa to 1 MPa in terms of the absolute pressure.

[0140]

In the case of this reaction, the fumaric acid ester derivative represented by formula (9) may remain in the product depending on the charged ratio to the alcohol, however, the product can be used without removing it.

[0141]

The fumaric acid ester derivative represented by formula (6) may also be obtained by once synthesizing a compound where a part of the fumaric acid ester of the fumaric acid ester derivative represented by formula (6) is maleic acid ester, and isomerizing the compound.

[0142]

The maleic acid ester derivative used for this isomerization reaction can be synthesized by a transesterification reaction of a maleic acid diester corresponding to the fumaric acid ester derivative represented by formula (9) with a polyhydric alcohol, similarly to the production method of the fumaric acid ester derivative represented by formula (6).

[0143]

The catalyst for use in the isomerization reaction from maleate to fumarate is preferably a complex of an element such as palladium, rhodium or ruthenium, or a supported catalyst comprising a support having supported thereon such an element. Particularly, in the case of purifying the fumaric acid ester derivative, a supported catalyst is preferably used in view of removal of the catalyst.

[0144]

The support for use in such a supported catalyst is not particularly limited and a porous substance commonly used as a catalyst may be used. Specific examples thereof include silica, alumina, silica alumina, zeolite, activated carbon, titania, magnesia and other inorganic compounds.

[0145]

The amount of the element supported on a support is preferably from 0.05 to 20% by mass, more preferably from 2 to 10% by mass, based on the entire amount of the catalyst. If the supported amount is less than 0.05% by mass, the reaction takes a time, whereas if it exceeds 20% by mass, the element not participating in the isomerization reaction disadvantageously increases.

[0146]

The thus-obtained supported catalyst is preferably

used in an amount of 0.01 to 50% by mass, more preferably from 1 to 30% by mass, based on the maleic acid ester. If the amount used is less than 0.01% by mass, the reaction takes a time, whereas if it exceeds 50% by mass, the catalyst not participating in the isomerization reaction disadvantageously increases. The isomerization reactions can be used individually or in combination of two or more thereof.

[0147]

The temperature at the isomerization reaction is not particularly limited. The isomerization reaction temperature is generally from 30 to 200°C, preferably from 60 to 180°C, more preferably from 80 to 160°C. If the reaction temperature is less than 30°C, the reaction proceeds slowly, whereas if it exceeds 200°C, polymerization may occur during the isomerization and this is not preferred.

[0148]

In the present invention, the isomerization reaction may also be performed in a solvent. Examples of the solvent which can be used include aromatic hydrocarbons such as benzene, toluene and xylene; ethers such as diethyl ether, dimethoxyethane, methoxyethyl ether, tetrahydrofuran and 1,4-dioxane; esters such as ethyl acetate and butyl acetate; ketones such as acetone and methyl ethyl ketone;

and alcohols such as methanol, ethanol and isopropanol. In the case of using a solvent, these solvents may be used in combination of two or more thereof.

[0149]

In the present invention, the isomerization reaction may be performed under atmospheric pressure or applied pressure, for example, at a pressure of 1 KPa to 1 MPa.

[0150]

During the transesterification reaction and the isomerization reaction, a polymerization inhibitor may also be added for preventing occurrence of polymerization.

[0151]

Examples of the polymerization inhibitor include quinones such as p-benzoquinone, naphthoquinone and 2,5-diphenyl-p-benzoquinone; polyhydric phenols such as hydroquinone, p-tert-butylcatechol or 2,5-di-tert-butylhydroquinone; and phenols such as hydroquinone monomethyl ether, di-tert-butyl paracresol and α -naphthol.

[0152]

The method for producing the fumaric acid ester derivative represented by formula (7) of the present invention (II), where R^1 is structural formula (1), is described below.

[0153]

The fumaric acid ester derivative represented by

formula (7) where R^1 is structural formula (1) can be produced by a transesterification reaction between the fumaric acid ester derivative represented by formula (10) and the polyhydric alcohol represented by formula (11).

[0154]

To speak more specifically, the fumaric acid ester derivative represented by formula (10) can be produced by performing an addition reaction of an ethylene glycol allyl ether or a propylene glycol allyl ether corresponding to R^1-O-X^1-OH with an epoxy compound having the X^3 unit, such as ethylene oxide, propylene oxide or cyclohexene oxide, to synthesize a corresponding alcohol, and then an esterification reaction with a fumaric acid or a transesterification reaction with a fumaric acid dialkyl ester.

[0155]

With respect to the polyhydric alcohol represented by formula (11), a corresponding polyhydric alcohol can be produced by an addition reaction of an ethylene glycol or a propylene glycol corresponding to $HO-X^2-OH$, with an epoxy compound having the X^3 unit, such as ethylene oxide, propylene oxide or cyclohexene oxide.

[0156]

In the forgoing pages, the step A) of forming an ester as the main skeleton of the fumaric acid ester derivative

and forming a repeating unit of the ester is described.

[0157]

The step B) of forming a polymerizable group at the terminal by isomerization is described below.

[0158]

The fumaric acid ester derivative represented by formula (5) of the present invention (I), where R^5 is structural formula (2), can be produced by a method of isomerizing the terminal group of the above-described fumaric acid ester derivative represented by formula (5) where R^5 is structural formula (1).

[0159]

Also, the fumaric acid ester derivative represented by formula (6) of the present invention (II), where R^1 is structural formula (2), and the fumaric acid ester derivative represented by formula (7) of the present invention (II), where R^1 is structural formula (2), can be produced by isomerizing respective corresponding fumaric acid ester derivatives where R^1 is structural formula (1).

[0160]

The isomerization reaction is described below.

The isomerization reaction from structural formula (1) to structural formula (2) can be performed using a known complex of an element such as palladium, rhodium or ruthenium, or using a supported catalyst comprising a

support having supported thereon such an element.

[0161]

The support for use in the supported catalyst is not particularly limited and a porous substance generally used as the support may be used. Specific examples thereof include silica, alumina, silica alumina, zeolite, activated carbon, titania, magnesia and other inorganic compounds.

[0162]

The amount of the element supported on a support is preferably from 0.05 to 20% by mass, more preferably from 2 to 10% by mass, based on the entire amount of the catalyst. If the amount supported is less than 0.05% by mass, the reaction takes a time, whereas if it exceeds 20% by mass, the element not participating in the isomerization reaction disadvantageously increases.

[0163]

The thus-obtained supported catalyst is preferably used in an amount of 0.01 to 50% by mass, more preferably from 1 to 30% by mass, based on the fumaric acid ester derivative represented by formula (5), (6) or (7) containing structural formula (1). If the amount of the catalyst is less than 0.01% by mass, the reaction takes a time, whereas if it exceeds 50% by mass, the catalyst not participating in the isomerization reaction disadvantageously increases. The isomerization reaction catalysts

may be used individually or in combination of two or more thereof.

[0164]

In the isomerization reaction, the reaction temperature is not particularly limited and is generally from 30 to 200°C, preferably from 60 to 180°C, more preferably from 80 to 160°C. If the reaction temperature is less than 30°C, the reaction takes a time, whereas if it exceeds 200°C, polymerization may occur during the isomerization and this is not preferred.

[0165]

In the present invention, the isomerization reaction may be performed in a solvent. Examples of the solvent which can be used include aromatic hydrocarbons such as benzene, toluene and xylene; ethers such as diethyl ether, dimethoxyethane, methoxyethyl ether, tetrahydrofuran and 1,4-dioxane; esters such as ethyl acetate and butyl acetate; ketones such as acetone and methyl ethyl ketone; alcohols such as methanol, ethanol and isopropanol. In the case of using a solvent, these solvents may be used in combination of two or more thereof.

[0166]

In the present invention, the isomerization reaction may be performed under atmospheric pressure or applied pressure, for example, at a pressure of 1 KPa to 1 MPa.

[0167]

In order to prevent occurrence of polymerization during the isomerization reaction, a polymerization inhibitor may also be added. Examples of the polymerization inhibitor include quinones such as p-benzoquinone, naphthoquinone and 2,5-diphenyl-p-benzoquinone; polyhydric phenols such as hydroquinone, p-tert-butylcatechol or 2,5-di-tert-butylhydroquinone; and phenols such as hydroquinone monomethyl ether, di-tert-butyl paracresol and α -naphthol.

[0168]

The present invention (IV) is described below.

The present invention (IV) is a polymerizable composition comprising the fumaric acid ester derivative of the present invention (I) or (II).

[0169]

The polymerizable composition of the present invention (IV) may contain, if desired, a compound having radical polymerizability or a radical polymerization initiator in addition to the fumaric acid ester derivative of the present invention (I) or (II).

[0170]

Examples of the radical polymerizable compound include unsaturated polyester, oligomer having (meth)acrylate, and radical polymerizable monomer.

[0171]

The unsaturated polyester is obtained by a polycondensation reaction of an α,β -unsaturated polybasic acid or an acid anhydride with a saturated polybasic acid and a polyhydric alcohol.

[0172]

Examples of the unsaturated polybasic acid include maleic acid, fumaric acid, itaconic acid, maleic anhydride and itaconic anhydride. Examples of the saturated polybasic acid used in combination as an acid component include saturated aliphatic dicarboxylic acids such as succinic acid, adipic acid and sebacic acid; aromatic polycarboxylic acids such as phthalic anhydride, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic anhydride and 2,6-naphthalene dicarboxylic acid; and alicyclic dicarboxylic acids such as endic anhydride, 1,2-cyclohexanedicarboxylic acid, hexahydrophthalic anhydride and 1,4-cyclohexanedicarboxylic acid. Examples of the polyhydric alcohol include aliphatic diols such as ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, dipropylene glycol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, 2-methyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, 1,6-nonanediol and 1,9-nonanediol; alicyclic diols such as 1,4-cyclohexanedimethanol, tricyclodecanedimethanol and

hydrogenated bisphenol A; aromatic diols such as ethylene oxide or propylene oxide adducts of bisphenol A; and trihydric or greater polyhydric alcohols such as glycerol, trimethylolpropane, trimethylolethane, pentaerythritol, sorbitol and dipentaerythritol.

[0173]

Other examples of the unsaturated polyester include those obtained by a transesterification reaction of the above-described saturated polybasic acid with a dialkyl ester of the unsaturated polybasic acid and the polyhydric alcohol. In this case, the alkyl group is usually a methyl group, an ethyl group, a propyl group or a butyl group.

[0174]

The (meth)acrylate-base compound for use in the present invention is a compound having two or more (meth)acryloyl group in the structure and specifically, can be obtained by a reaction of a urethane (meth)acrylate, a polyhydric alcohol, a polybasic acid or an anhydride thereof, and a (meth)acrylic acid.

[0175]

Specific examples thereof include polyester (meth)acrylates, polyether (meth)acrylates obtained by reacting a polyhydric alcohol resulting from addition of ethylene oxide or propylene oxide to a hydroxyl group-containing compound with a (meth)acrylic acid, epoxy

(meth)acrylates obtained by reacting an epoxy compound with a (meth)acrylic acid or a (meth)acrylate having a carboxyl group, polyfunctional (meth)acrylates such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, glycerol di(meth)acrylate, trimethylolethane tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate and dipentaerythritol hexa(meth)acrylate, and silicon (meth)acrylates having a siloxane group and a (meth)acryloyl group.

[0176]

The urethane (meth)acrylate for use in the present invention is known and can be obtained by reacting a polyhydric alcohol, a polyisocyanate and a hydroxyethyl (meth)acrylate or hydroxypropyl (meth)acrylate. Examples of the polyhydric alcohol include those described above for the polyhydric alcohol of the unsaturated polyester. Examples of the polyisocyanate include toluene diisocyanate, 4,4'-diphenylmethane isocyanate, xylene diisocyanate, hexamethylene diisocyanate and isophorone diisocyanate.

[0177]

Examples of the polybasic acid and the polyhydric alcohol used as starting materials of the polyester (meth)acrylate or polyether (meth)acrylate for use in the

present invention include those described above with respect to the unsaturated polyester.

[0178]

Known examples of the epoxy compound used as a starting material of the epoxy (meth)acrylate for use in the present invention include epoxy resin-base compounds such as glycidyl ether of bisphenols (e.g., bisphenol A, bisphenol S, bisphenol F), and novolak-type glycidyl ether.

[0179]

The radical polymerizable monomer for use in the present invention has a double bond as a polymerizable group. Specific examples thereof include monofunctional (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate and isobornyl (meth)acrylate; aromatic vinyl compounds such as styrene, α -styrene, methoxy styrene and divinylbenzene; vinyl esters of aliphatic carboxylic acid, such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate, vinyl stearate and vinyl caproate; alicyclic vinyl esters such as vinyl ester of cyclohexanecarboxylic acid; vinyl esters of aromatic acid, such as vinylbenzoate and tert-butyl vinylbenzoate; hydroxyalkyl vinyl esters such as hydroxyethyl vinyl ester, hydroxypropyl vinyl ester and hydroxybutyl vinyl ester;

allyl compounds such as diallyl phthalate, diallyl isophthalate, diallyl terephthalate, diallyl maleate, diallyl fumarate, diallyl itaconate, diallyl trimellitate, triallyl cyanurate, triallyl isocyanurate, diallyl carbonate, diethylene glycol bisallyl carbonate, trimethylol propane diallyl ether and pentaerythritol triallyl ether; maleimides such as N-methylmaleimide, N-cyclohexylmaleimide, N-phenylmaleimide, N-laurylmaleimide, N-2-methylphenylmaleimide, N-2-chlorophenylmaleimide, N-2-methoxyphenylmaleimide, N,N-4,4'-diphenylmethane bismaleimide; unsaturated dibasic acids and derivatives thereof, such as maleic acid, fumaric acid, maleic anhydride, dimethyl maleate, diethyl maleate, dimethyl fumarate, diethyl fumarate, dimethyl itaconate and diethyl itaconate; and the fumaric acid ester derivatives represented by formulae (9) and (10).

[0180]

Particularly, when the fumaric acid ester derivative represented by formula (9) or (10) is used and blended, the polymerizable composition of the present invention (IV) is not prone to curing inhibition by oxygen and can have good surface curability. These radical polymerizable monomers can be used individually or in combination of two or more thereof.

[0181]

The amount of the fumaric acid ester derivative of the present invention (I) or (II) used in the polymerizable composition of the present invention (IV) is from 1 to 99% by mass, preferably from 5 to 80% by mass, in the curable composition. In particular, when the amount used is 5% by mass or more, the polymerizable composition is scarcely affected by the curing inhibition due to oxygen and can be prevented from occurrence of surface stickiness.

[0182]

The radical polymerization initiator which can be used for the polymerizable composition of the present invention (IV) may be any radical polymerization initiator as long as it can generate a radical, for example, by heat, ultraviolet ray, electron beam or radiation.

[0183]

Examples of the radical polymerization initiator which can be used in the radical polymerization by heat include azo-base compounds such as 2,2'-azobisisobutyronitrile and 2,2'-azobisisovaleronitrile; ketone peroxides such as methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide and cyclohexanone peroxide; diacyl peroxides such as benzoyl peroxide, decanoyl peroxide and lauroyl peroxide; dialkyl peroxides such as dicumyl peroxide, tert-butylcumyl peroxide and di-tert-butyl peroxide; peroxy

ketals such as 1,1-di-tert-butylperoxy cyclohexane and 2,2-di(tert-butylperoxy)butane; alkyl peresters such as tert-butylperoxy pivalate, tert-butylperoxy-2-ethyl hexanoate, tert-butylperoxy isobutylate, di-tert-butylperoxy hexahydroterephthalate, di-tert-butylperoxy azelate, tert-butylperoxy-3,5,5-trimethyl hexanoate, tert-butylperoxy acetate, tert-butylperoxy benzoate and di-tert-butylperoxy trimethyladipate; and percarbonates such as diisopropylperoxy dicarbonate, di-sec-butylperoxy dicarbonate and tert-butylperoxy isopropylcarbonate.

[0184]

In the film formation such as coating by heat, it is also possible to cause self-crosslinking without using a radical polymerization initiator.

[0185]

Examples of the radical polymerization initiator which can be used for the polymerization by ultraviolet ray or electron beam include acetophenone derivatives such as acetophenone, 2,2-dimethoxy-2-phenylacetophenone, diethoxyacetophenone, 1-hydroxy-cyclohexyl-phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 and 2-hydroxy-2-methyl-1-phenyl-propan-1-one; benzophenone derivatives such as benzophenone, 4,4'-bis(dimethylamino)benzophenone, 4-trimethylsilylbenzophenone and 4-

benzoyl-4'-methyl-diphenylsulfide; benzoin derivatives such as benzoin, benzoin ethyl ether, benzoin propyl ether, benzoin isobutyl ether and benzoin isopropyl ether; methyl phenyl glyoxylate; benzoin dimethyl ketal; and 2,4,6-trimethylbenzoyldiphenylphosphine oxide.

[0186]

The amount of the polymerization initiator used is from 0.01 to 15% by mass, preferably from 0.1 to 10% by mass, based on the weight of the polymerizable composition of the present invention (IV).

[0187]

In the case of polymerizing the polymerizable composition of the present invention, various additives may be added according to the use end. Examples of the additives which can be used in combination include ultraviolet absorbent, antioxidant, coloring agent, lubricant, antistatic agent and inorganic filler such as silica, alumina and aluminum hydroxide.

[0188]

The polymerizable composition of the present invention (IV) can be cured by a curing method using ultraviolet ray, electron beam or heat, such as coating by means of roll coater or spin coater, cast formation or photoformation.

[0189]

Depending on the curing method, when the viscosity of

the polymerizable composition of the present invention must be lowered, a solvent may be used. Examples of the solvent which can be used include aromatic hydrocarbons such as toluene and xylene; acetic acid esters such as methyl acetate, ethyl acetate, propyl acetate and butyl acetate; ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone; ethers such as tetrahydrofuran and dioxane; and alcohols such as ethyl alcohol, (iso)propyl alcohol and butyl alcohol.

[0190]

The present invention (V) is described below. The present invention (V) is a cured product obtained by curing the polymerizable composition of the present invention (IV).

[0191]

The cured product of the present invention (V) can be used over a wide range in the field of curable resin, for example, coating materials such as wood coating, film coating, metal coating, plastic coating, inorganic coating, hard coating, optical fiber coating and gel coating agent; painting materials such as coating or printing ink; optical materials such as photoformation material, optical disk, spectacle lens and prism; adhesive; photoresist; sealant; and molding materials. The cured product of the present invention (V) is useful particularly as a coating material for forming a thin film which is prone to inhibition by

oxygen. The substrate subjected to the coating is not particularly limited. Specific examples thereof include metal, glass and plastic.

[0192]

The resin obtained by curing the polymerizable composition of the present invention has a high crosslinking density and therefore, a cured product having a high surface hardness can be obtained. In particular, a cured resin of the fumaric acid ester derivative having a tri-, tetra-, hepta- or hexa-hydric alcohol in the skeleton, represented by formula (5), has a surface hardness as high as 4H to 8H in terms of the pencil hardness (JIS K-5400) and therefore, can be optimally used in the field where abrasion resistance or scratch resistance is required.

[0193]

[Examples]

The present invention is described in greater detail below by referring to the Examples, however, the present invention should not be construed as being limited to these Examples as long as the spirit of the present invention is observed.

[0194]

In the measurements of various data, the following instruments were used.

(Instruments Used)

¹H-NMR

Model of instrument used: JEOL EX-400 (400 MHz)

A sample was dissolved in chloroform deuteride and measured using tetramethylsilane as the internal standard substance, and a chemical shift was calculated.

FT-IR

Model of instrument used:

Spectrum GX manufactured by Perkin-Elmer

The measurement was performed by a liquid film method using KBr plate.

[0195]

GPC

Model of instrument used:

pump: Shodex DS-4, UV detector: Waters 484,

RI detector: Shodex RI SE-61

Column used:

Shodex K-G+K-801 (in Example 1, K-802 was added)

Measuring conditions:

eluent: chloroform, flow rate: 1 ml/min.,

column temperature: 40°C, detection: UV 254 nm

GC (monomer analysis)

Model of instrument used:

GC-14B (manufactured by Shimadzu Seisakusho)

Column used:

DB-23, 0.25 μ \times 30 m (manufactured by J & W)

Carrier gas: nitrogen, 1 ml/min.

Split ratio: 1:50

Septum purge: 10 ml/min.

Detector: FID

Injection temperature: 230°C

Detector temperature: 230°C

Temperature program:

40°C (10 min.) \rightarrow (10°C/min.) \rightarrow 200°C

UV irradiation apparatus

Model of instrument used:

TOSCURE 401 (manufactured by Toshiba K.K.),

Light source: mercury lamp,

Irradiation intensity:

irradiation distance: 100 mm - 70 mW/cm²

[0196]

(Example 1)

Into a 1 L-volume flask equipped with a distillation unit, 312 g of bis(2-allyloxyethyl) maleate, 135 g of ethylene oxide 2-mol adduct of bisphenol A, 0.4 g of dibutyltin oxide and 0.12 g of tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane ("IRGANOX 1010", trade name, produced by Chiba Specialty Chemicals) as a polymerization initiator were charged. While gradually

reducing the pressure inside the reaction system, the mixture was heated at 160°C and ethylene glycol monoallyl ether generated as a by-product was distilled off. Finally, the pressure was reduced to about 400 Pa and a nearly theoretical amount of ethylene glycol monoallyl ether was distilled off.

[0197]

After cooling the reaction solution to room temperature, 385 g of the product was taken out. ¹H-NMR and IR of the product obtained were measured and this product was identified as a condensate of bis(2-allyloxyethyl) maleate with ethylene oxide 2-mol adduct of bisphenol A.

[0198]

By the GC analysis, the product was found to contain 30.3% of bis(2-allyloxyethyl) maleate.

[0199]

¹H-NMR

δ(ppm): 7.13-7.11 (m, Ph), 6.81-6.78 (m, Ph), 6.29 (s, -OCOCH=CHCOO-), 5.95-5.84 (m, CH₂=CH-CH₂-), 5.31-5.25 (m, CH₂=CH-CH₂-), 5.21-5.17 (m, CH₂=CH-CH₂-), 4.52-3.64 (m, -O-CH₂-CH₂-COO-, CH₂=CH-CH₂-, -O-CH₂-CH₂-COO-, Ph-O-CH₂-CH₂-OCO-C=C-), 1.63 (s, Ph-C(Me)₂-Ph), 1.62 (Ph-C(Me)₂-Ph).

IR

$\nu(\text{CO})=1,733 \text{ cm}^{-1}$, $\nu(\text{allyl C=C, maleate C=C})=1,647 \text{ cm}^{-1}$

[0200]

62.4 g of the mixture obtained, 60 ml of toluene, 60 ml of 1-propanol and 6.2 g of Ru-C supported in an amount of 5% by mass were charged and after purging with nitrogen, the temperature was elevated to 150°C. Subsequently, the mixture was stirred under heating at the same temperature for 10 hours. After cooling, the catalyst was separated by filtration from the reaction solution and the solvent was distilled off under reduced pressure from the filtrate, as a result, 59.2 g of a highly viscous yellow liquid was obtained. By NMR, the isomerization ratio from the double bond of maleic acid residue ($\delta=6.29 \text{ ppm}$) to the double bond of fumaric acid residue ($\delta=6.93$ to 6.86 ppm) was 100%.

[0201]

The area percentage in the chart of analysis results by GPC of the product obtained is shown in Table 1 with respect to the condensation degree n (the number of repeating units) of the product.

[0202]

[Table 1]

Condensation degree n	0	1	2	3	≥ 4
Composition (area %)	30.3	29.0	23.1	13.0	4.6

[0203]

(Example 2)

Into a 3 L-volume glass flask, 500 g of maleic anhydride, 573 g of ethylene glycol monoallyl ether and 0.05 g of hydroquinone monomethyl ether were charged. The mixture was stirred under heating at 50°C for 24 hours in a nitrogen atmosphere. To the reactant obtained, 1 kg of 1,4-dioxane, 10 g of concentrated hydrochloric acid and 0.1 g of hydroquinone monomethyl ether were added and the mixture was stirred under heating at 100°C for 1 hour. Thereafter, 1,4-dioxane was distilled off under reduced pressure and to the reactant, 1 kg of toluene and 1 kg of water were added and liquid-separated. Toluene was distilled off under reduced pressure from the organic layer, as a result, 1,020 g of a pale yellow liquid was obtained. From the analyses by NMR and FT-IR, the product was identified as mono-2-allyloxyethyl fumarate.

[0204]

¹H-NMR

δ(ppm): 10.44 (br.s, 1H, -COOH), 7.30-6.83 (m, 2H, -OCOCH=CHCOO-), 5.92-5.88 (m, 1H, CH₂=CH-CH₂-), 5.32-5.21 (m, 2H, CH₂=CH-CH₂-), 4.37 (br.s, 2H, -O-CH₂-CH₂-COO-), 4.07 (br.s, 2H, CH₂=CH-CH₂-), 3.73 (br.s, 2H, -O-CH₂-CH₂-COO-).

IR

$\nu(\text{OH})=3,300-2,500 \text{ cm}^{-1}$, $\nu(\text{CO})=1,727 \text{ cm}^{-1}$, $\nu(\text{allyl C=C})=1,647 \text{ cm}^{-1}$

[0205]

(Example 3)

Into a 500 ml-volume glass flask equipped with a stirring unit, a thermometer, a condenser and a distilling receiver with stopcock, 154 g of mono-2-allyloxyethyl fumarate obtained in Example 2, 21.8 g of pentaerythritol, 200 ml of benzene and 0.25 g of p-toluenesulfonic acid were charged. The mixture was stirred under heating in an oil bath, the reaction temperature was elevated to 80°C and the reaction was continued while distilling off the water generated as a by-product with the progress of the reaction. When the amount of water distilled off reached the theoretical amount, the reaction was finished and the reaction solution was cooled. This reaction solution was transferred to a separatory funnel, 300 ml of benzene was added thereto, and the separation was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was concentrated under reduced pressure to obtain 120 g of a product.

[0206]

$^1\text{H-NMR}$, FT-IR, GC and GPC of the product were measured and this product was identified as a composition containing

a condensate of pentaerythritol with mono-2-allyloxyethyl fumarate, and 43% (by GC) of bis(2-allyloxyethyl) fumarate monomer.

IR

$\nu(\text{CO})=1,727 \text{ cm}^{-1}$, $\nu(\text{allyl C=C})=1,647 \text{ cm}^{-1}$

[0207]

(Example 4)

Into a 500 ml-volume glass flask equipped with a stirring unit, a thermometer, a condenser and a distilling receiver with stopcock, 152 g of mono-2-allyloxyethyl fumarate obtained in Example 3, 21.5 g of trimethylol propane, 200 ml of benzene and 0.25 g of p-toluenesulfonic acid were charged. The mixture was stirred under heating in an oil bath, the reaction temperature was elevated to 80°C, and the reaction was continued while distilling off the water generated as a by-product with the progress of the reaction. When the amount of water distilled off reached the theoretical amount, the reaction was finished and the reaction solution was cooled. This reaction solution was transferred to a separatory funnel, 300 mL of benzene was added thereto, and the separation was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was concentrated under reduced pressure to obtain 118 g of a product.

[0208]

¹H-NMR, FT-IR, GC and GPC of the product were measured and this product was identified as a composition containing a condensate of trimethylol propane with mono-2-allyloxyethyl fumarate, and 30% (by GC) of bis(2-allyloxyethyl) fumarate monomer.

IR

$\nu(\text{CO})=1,727 \text{ cm}^{-1}$, $\nu(\text{allyl C=C})=1,647 \text{ cm}^{-1}$

[0209]

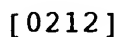
(Example 5)

Into a 3 L-volume glass flask, 500.7 g of mono-2-allyloxyethyl fumarate obtained in Example 3 and 1.8 kg of THF were charged. The inside of the reaction system was purged with nitrogen and then 345.5 g of potassium carbonate was added. After the completion of heat generation, the mixture was stirred for 1 hour and the reaction solution was cooled with ice water. Separately, a THF solution was prepared by dissolving 524.3 g of p-toluenesulfonyl chloride in 200 g of THF. When the temperature of the reaction solution reached 10°C or less, the prepared p-toluenesulfonyl chloride/THF solution was added thereto and stirred for 30 minutes. Thereafter, 70.9 g of pentaerythritol and 691.1 g of potassium carbonate were added and stirred. After the completion of heat generation, the ice water was removed and the reaction

[0210]

[0211]

[Chem. 41]



- 74 -

[0213]

[Table 2]

Value of k	4	3	$2 \geq$
Compositional ratio (area % by GPC)	88.3	2.2	9.5

[0214]

The mixture obtained above was subjected to thin layer chromatography ("Pre Coated PLC Plates SILICA GEL 60 F-254", produced by MERCK) in which silica was supported, using ethyl acetate/hexane=1/2 as the developer to isolate compounds having a k value of 4 or 3. These compounds were measured by NMR and the above-described mixture was re-identified.

[0215]

k=4

^1H -NMR

δ (ppm) 6.92 (d, 4H, $J=15.6\text{Hz}$, $-\text{OCOCH}=\text{CHCOO}-$), 6.85 (d, 4H, $J=15.6\text{Hz}$, $-\text{OCOCH}=\text{CHCOO}-$), 5.96-5.86 (m, 4H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 5.30 (d, 4H, $J=17.3\text{Hz}$, $J=1.47\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 5.22 (dd, 4H, $J=10.5\text{Hz}$, $J=1.47\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 4.38 (t, 8H, $J=4.6\text{Hz}$, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{COO}-$), 4.34 (s, 8H, $\text{C}-\text{CH}_2-$), 4.04 (d, 8H, $J=5.4\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 3.70 (t, 8H, $J=4.6\text{Hz}$, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{COO}-$).

IR

$\nu(\text{CO})=1,727\text{ cm}^{-1}$, $\nu(\text{allyl C}=\text{C})=1,647\text{ cm}^{-1}$

[0216]

k=3

¹H-NMR

δ(ppm) 6.92 (d, 3H, J=13.9Hz, -OCOCH=CHCOO-), 6.87 (d, 3H, J=13.9Hz, -OCOCH=CHCOO-), 5.96-5.86 (m, 3H, CH₂=CH-CH₂-), 5.30 (d, 3H, J=17.1Hz, CH₂=CH-CH₂-), 5.22 (d, 3H, J=10.3Hz, CH₂=CH-CH₂-), 4.38 (t, 6H, J=4.6Hz, -O-CH₂-CH₂COO-), 4.31 (s, 6H, C-CH₂-), 4.04 (d, 6H, J=5.9Hz, CH₂=CH-CH₂-), 3.70 (t, 6H, J=4.6Hz, -O-CH₂-CH₂-COO-) 3.63 (s, 2H, C-CH₂-).

IR

ν(CO)=1,727 cm⁻¹, ν(allyl C=C)=1,647 cm⁻¹

[0217]

(Example 6)

Into a 3 L-volume glass flask, 500.2 g of mono-2-allyloxyethyl fumarate obtained in Example 3 and 1.8 kg of THF were charged. The inside of the reaction system with nitrogen and then, 345.1 g of potassium carbonate was added. After the completion of heat generation, the mixture was stirred for 1 hour and the reaction solution was cooled with ice water. Separately, a THF solution was prepared by dissolving 524.3 g of p-toluenesulfonyl chloride in 200 g of THF. When the temperature of the reaction solution reached 10°C or less, the p-toluenesulfonyl chloride/THF

solution prepared was added and the reaction solution was stirred for 30 minutes. Thereafter, 93.2 g of trimethylolpropane and 691.0 g of potassium carbonate were added and stirred. After the completion of heat generation, the ice water was removed and the reaction solution was returned to room temperature and further stirred for 2 hours.

[0218]

Then, the reaction solution was concentrated, the concentrate was transferred to a separatory funnel, 2 kg of ethyl acetate was added, and the separation washing was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was concentrated under reduced pressure to obtain 267 g of a product. ^1H -NMR, FT-IR and GPC of the product were measured and this product was identified as a condensate of trimethylolpropane with mono-2-allyloxyethyl fumarate, represented by formula (13).

[0219]

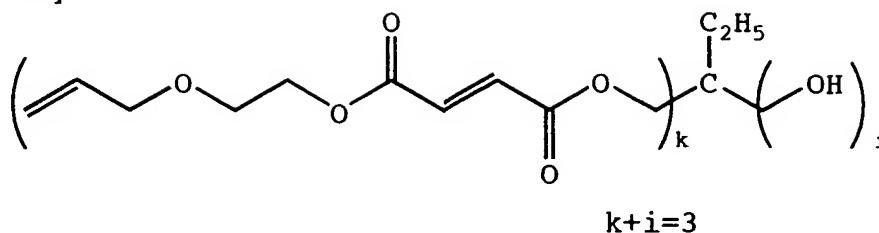
IR

$\nu(\text{CO})=1,727\text{ cm}^{-1}$, $\nu(\text{allyl C}=\text{C})=1,647\text{ cm}^{-1}$

[0220]

Formula (13)

[Chem. 42]



[0221]

The area percentage in the chart of analysis results by GPC of the product obtained is shown in Table 3 with respect to the value of k in formula (13).

[0222]

[Table 3]

Value of k	3	$2 \geq$
Compositional ratio (area % by GPC)	91.8	8.2

[0223]

(Example 7)

Into a 1 L-volume round bottom flask equipped with a magnetic spinbar, a magnetic stirrer, a Dimroth condenser and a nitrogen inducing tube, 118.19 g of cyclohexanediol monoallyl ether, 148.71 g of maleic anhydride, 268 mg of hydroquinone monomethyl ether and 363 g of toluene were charged, and the mixture was stirred under heating at 110°C for 24 hours in a nitrogen atmosphere. To the reactant obtained, 12.6 g of concentrated hydrochloric acid and

267 mg of hydroquinone monomethyl ether were added. The resulting mixture was heated under reflux for 5 hours in a nitrogen atmosphere and then cooled. The white precipitate deposited was separated by filtration through a 0.1 μ m membrane filter and the filtrate was separated with water (500 mL \times 3 times). The obtained organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure by an evaporator, as a result, 162.49 g of a pale yellow viscous liquid was obtained.

[0224]

Into a 500 mL-volume glass flask equipped with a stirring unit, a thermometer, a condenser and a distilling receiver with stopcock, 53.9 g of the pale yellow viscous liquid prepared above, 6.0 g of pentaerythritol, 50 mL of toluene, 811.8 mg of p-toluenesulfonic acid and 54.6 mg of hydroquinone monomethyl ether were charged. The mixture was heated under reflux in an oil bath and the reaction was continued while distilling off the water generated as a by-product with the progress of the reaction. When the amount of water distilled off reached the theoretical amount, the reaction was finished and the reaction solution was cooled. This reaction solution was transferred to a separatory funnel, 300 mL of ethyl acetate was added thereto, and the separation was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting

solution was dried over sodium sulfate and concentrated under reduced pressure to obtain 38.9 g of a product.

[0225]

¹H-NMR, FT-IR, GC and GPC of the product were measured and this product was identified as a composition containing a condensate of pentaerythritol with mono-2-allyloxycyclohexyl fumarate, and 40% (by GC) of bis(2-allyloxycyclohexyl) fumarate monomer.

[0226]

IR

$\nu(\text{CO})=1,723 \text{ cm}^{-1}$, $\nu(\text{allyl C}=\text{C})=1,645 \text{ cm}^{-1}$

[0227]

(Example 8)

Into a 1 L-volume round bottom flask equipped with a magnetic spinbar, a magnetic stirrer, a Dimroth condenser and a nitrogen inducing tube, 118.19 g of cyclohexanediol monoallyl ether, 148.71 g of maleic anhydride, 268 mg of hydroquinone monomethyl ether and 363 g of toluene were charged, and the mixture was stirred under heating at 110°C for 24 hours in a nitrogen atmosphere. To the reactant obtained, 12.6 g of concentrated hydrochloric acid and 267 mg of hydroquinone monomethyl ether were added. The resulting mixture was heated under reflux for 5 hours in a nitrogen atmosphere and cooled and the white precipitate deposited was separated by filtration through a 0.1 μm

membrane filter. The filtrate was separated with water (500 mL × 3 times) and the obtained organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure by an evaporator, as a result, 162.49 g of a pale yellow viscous liquid was obtained.

[0228]

Into a 3 L-volume glass flask, 60.8 g of the pale yellow viscous liquid obtained above and 200 mL of THF were charged. The inside of the reaction system was purged with nitrogen and then 22 g of potassium carbonate was added. After the completion of heat generation, the mixture was stirred for 1 hour and the reaction solution was cooled with ice water. When the temperature of the reaction solution reached 10°C or less, 7.6 g of p-toluenesulfonyl chloride was added and stirred for 30 minutes. Thereafter, 5.4 g of pentaerythritol were added and stirred. The reaction solution was returned to room temperature and stirred for 12 hours. Then, the reaction solution was concentrated, the concentrate was transferred to a separatory funnel, 500 mL of ethyl acetate was added, and the separation washing was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was concentrated under reduced pressure to obtain 30 g of a product. ¹H-NMR, FT-IR and GPC of the product were measured and the product was identified as a

condensate of pentaerythritol with mono-2-allyloxycyclohexyl fumarate, represented by formula (14).

[0229]

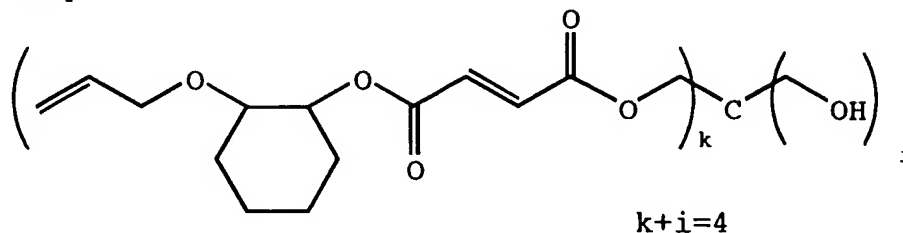
IR

$\nu(\text{CO})=1,723 \text{ cm}^{-1}$, $\nu(\text{allyl C}=\text{C})=1,645 \text{ cm}^{-1}$

[0230]

Formula (14)

[Chem. 43]



[0231]

The area percentage in the chart of analysis results by GPC of the product obtained is shown in Table 4 with respect to the value of k in formula (14).

[0232]

[Table 4]

Value of k	4	3	$2 \geq$
Compositional ratio (area % by GPC)	82.2	2.0	15.8

[0233]

(Examples 9 to 14)

50 g of the mixture obtained in Example 3, 50 g of toluene, 10 mg of hydroquinone monomethyl ether (MEHQ) and 15 g of 5% Pd-Al₂O₃ were added and after purging the inside

of the reaction system with nitrogen, the mixture was stirred under heating at 140°C for 3 hours. After cooling, 5% Pd-Al₂O₃ was removed by filtration from the reaction solution and then toluene was distilled off under reduced pressure from the filtrate to obtain 48 g of a pale yellow viscous liquid. ¹H-NMR was measured and by comparing the peaks of ally group and propenyl group, it was confirmed that 98% was isomerized into propenyl group.

[0234]

The isomerization reaction of the mixtures obtained in Examples 4, 5, 6, 7 and 8 was performed by the same operation. The results shown together in Table 5.

[0235]

[Table 5]

Example	Charging					Reaction Results
	Example where Starting Material used for Reaction is described	Starting Material (g)	Toluene (g)	Catalyst (g)	MEHQ (mg)	Isomerization ratio (%)
9	3	50	50	15	10	98
10	4	50	50	15	10	100
11	5	85	85	25	18	100
12	6	50	50	15	10	98
13	7	50	50	15	10	98
14	8	50	50	15	10	99

[0236]

(Examples 15 to 24)

The fumaric acid ester derivatives of the present invention obtained in the Examples above each was coated on a glass substrate and cured by UV or heat. The surface hardness of the cured film was examined. The surface hardness was determined in accordance with the pencil scratch test of JISK 5400.

[0237]

The results are shown in Table 6.

[0238]

[Table 6]

	Fumaric Acid Ester Derivative	Curing Method	Curing Conditions		Pencil Hard- ness
			Initiator	temperature- Time/UV Exposure	
Example 15	Compound of Example 1	heat	none	150°C-1 h	5H
Example 16	Compound of Example 3	heat	none	150°C-1 h	6H
Example 17	Compound of Example 4	heat	DCP ¹⁾ 2%	150°C-0.5 h	6H
Example 18	Compound of Example 5	heat	DCP ¹⁾ 2%	150°C-0.5 h	7H
Example 19	Compound of Example 6	UV	IRG184 ²⁾ 5%	900 mj/cm ²	6H
Example 20	Compound of Example 8	heat	none	150°C-1 h	7H
Example 21	Compound of Example 9	UV	IRG184 ²⁾ 5%	300 mj/cm ²	7H
Example 22	Compound of Example 10	UV	IRG184 ²⁾ 5%	300 mj/cm ²	6H
Example 23	Compound of Example 11	UV	IRG184 ²⁾ 5%	300 mj/cm ²	7H
Example 24	Compound of Example 11	heat	none	150°C-1 h	8H
Example 25	Compound of Example 12	heat	none	150°C-1 h	7H
Example 26	Compound of Example 14	UV	IRG184 ²⁾ 5%	300 mj/cm ²	7H
Comparative Example 1	Compound of Comparative Example 1	UV	IRG184 ²⁾ 5%	1200 mj/cm ²	HB
Comparative Example 2	Compound of Comparative Example 2	heat	DCP ¹⁾ 2%	150°C-1 h	2H

1) DCP : dicumyl peroxide

2) IRG184 : IRGACURE 184 (1-hydroxy-cyclohexyl-phenyl-ketone),
trade name, produced by Ciba Specialty Chemicals

[0239]

(Comparative Example 1)

Into a 1 L-volume flask equipped with a distillation unit, 144 g of dimethyl fumarate, 245 g of ethylene glycol monoallyl ether, 0.2 g of dibutyltin oxide were charged. The mixture was heated at 140°C in a nitrogen atmosphere and methanol generated as a by-product was distilled off. When methanol reached 70% of the theoretical amount, the pressure inside the reaction system was gradually reduced to accelerate the distillation of methanol, and by finally reducing the pressure to about 400 Pa, the theoretical amount of methanol and the residual ethylene glycol monoallyl ether were completely distilled off. The reaction solution was cooled to room temperature and then 283 g of a product was taken out. ¹H-NMR and FT-IR of the product obtained were measured and this product was identified as bis(2-allyloxyethyl) fumarate.

[0240]

This product was coated on a glass substrate and cured by UV. The surface hardness of the cured film was examined. The surface hardness was determined in accordance with the pencil scratch test of JISK 5400.

The results are shown in Table 6.

[0241]

(Comparative Example 2)

Into a 1 L-volume flask equipped with a distillation unit, 144 g of dimethyl fumarate, 279 g of hydroxybutyl vinyl ether, 0.2 g of zinc acetate and 0.3 g of IRGANOX 1010 as a polymerization inhibitor were charged. The mixture was heated to 140°C in a nitrogen atmosphere and methanol generated as a by-product was distilled off. When methanol reached 70% of the theoretical amount, the pressure inside the reaction system was gradually reduced pressure to accelerate the distillation of methanol, and by finally reducing the pressure to about 400 Pa, the theoretical amount of methanol and the residual hydroxybutyl vinyl ether were completely distilled off. The reaction solution was cooled to room temperature and then 297 g of bis(4-vinyloxybutyl) maleate was obtained.

[0242]

This product was coated on a glass substrate and cured by UV. The surface hardness of the cured film was examined. The surface hardness was determined in accordance with the pencil scratch test of JISK 5400.

The results are shown in Table 6.

[0243]

(Examples 27 to 33)

A composition of the fumaric acid ester derivative of

the present invention was coated on a PET film or a glass substrate and cured by UV or heat. The surface hardness of the cured film was examined. The tack-free coating having no tackiness on the cured surface was rated ○ and the coating having tackiness was rated ×.

[0244]

The curing was performed under the following conditions.

① Heat curing

Temperature 150°C-1 hour

② UV curing

Initiator: IRGACURE-184, 5%

Exposure: 300 mj/cm²

The results are shown in Table 7.

[0245]

[Table 7]

	Example 27	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33	Comparative Example 3	Comparative Example 4
Blending, % by weight	Compound of Example 1	50	50	80	50	80	60	100	100
	Compound of Example 10								
	Compound of Example 11								
	Compound of Example 12								
	PE-TA ³⁾								
	80MFA ⁴⁾								
	8524 ⁵⁾								
	BPF ⁶⁾	30	50	20	50	20	20	100	100
Curing Method		①	①	①	②	②	②	①	②
Film Properties	Tack	○	○	○	○	○	○	×	○
	Pencil hardness	5H	6H	7H	6H	2H	2H	-	F
Substrate		glass	glass	glass	glass	PET	PET	glass	PET

3) PE-TA: pentaerythritol triacrylate,

4) Epoxy Ester 80MFA: epoxy acrylate, trade name, produced by Kyoei-Sha Kagaku

5) Unsaturated Polyester 8524: trade name, produced by Nippon Yupica K.K.

6) BPF: bis[2-(1-propenyloxy)ethyl fumarate

[0246]

[Effects of the Invention]

As described in the foregoing pages, the fumaric acid ester derivative of the present invention has two or more fumarate groups within one molecule and the copolymerizability with the terminal alkenyloxy group is high as compared with conventional fumaric acid ester derivatives, so that the crosslinking degree can increase and a cured product having excellent surface hardness can be provided. Also, the composition thereof with other polymerizable compounds can be used similarly for the purpose of improving the curability and elevating the surface hardness.

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a polymerizable composition having excellent curability and surface hardness, and a cured product thereof.

[MEANS TO SOLVE THE PROBLEM]

A novel fumaric acid ester derivative having two or more fumarate groups within one molecular and ensuring high copolymerizability with the terminal alkenyloxy group, a method for producing the derivative, a polymerizable composition containing the derivative, and a cured product thereof are provided.

[SELECTED DRAWING] None.